Static displacements and chemical correlations in alloys

Bulbul Chakraborty

The Martin Fisher School of Physics

Brandeis University

Waltham, MA 02254, USA

Abstract

Recent experiments in metallic solid solutions have revealed interesting correlations between static pair-displacements and the ordering behavior of these alloys. This paper discusses a simple theoretical model which successfully explains these observations and which provides a natural framework for analyzing experimental measurements of pair-displacements and chemical correlations in solid solutions. The utility and scope of this model is demonstrated by analyzing results of experiments on $Ni-Fe$ and $Cr-Fe$ alloys and results of simulations of $Cu-Au$ and $Cu-Ag$ alloys.

Metallic alloys which exist as crystalline solid solutions at high temperature are classified, according to their low-temperature behavior, as ordering or clustering alloys. Investigation of the local correlations in the high-temperature phase yields important information regarding the low-temperature behavior and is an extensively used tool in the study of alloy phase stability. Measurements of chemical correlations have been used to extract effective interaction parameters in theoretical models [1]. In recent experiments, the measurements were extended to include chemically specific *displacements* of atoms [1,2]. A striking observation of these experiments was a correlation between AB distances and the clustering or ordering tendency of the $A-B$ alloy [2]. It was observed that the AB distances were the shortest distances in an ordering alloy; contrary to expectations based on "size-effect" arguments [1,2].

The purpose of this paper is to present a theoretical model which successfully explains the correlation between pair-displacements and the ordering behavior of alloys. The most important predictions of this model are: (i) the AB distances are always shorter than the arithmetic mean of the AA and BB distances in an ordering alloy and larger than the arithmetic mean in a clustering alloy and (ii) the AB distances are the *shortest* in an ordering alloy where the size difference is negligible. This model is the first of its kind to lead to these predictions, especially the second, and identifies the types of interactions needed to understand the experimental observations. Simulations of alloys with large size differences follow the trend of prediction (i) as demonstrated by embedded atom studies [3,4].

The model under discussion is a compressible Ising model [5], extended to include size-effect terms which are non-existent in a magnetic system but can be extremely important in binary alloys. This model is referred to as the generalized Ising model in the following. The compressible Ising model provides a simple description of order-disorder transitions in alloys which are accompanied by a displacive structural transition [6,7]. An example is the ordering transition in $CuAu$ which is accompanied by a cubic to tetragonal distortion [6,8]. The present work shows that this model provides a good description of displacements in binary alloys including transition metal alloys whose microscopic interactions are very different

from those of $Cu - Au$ alloys. The generalized Ising model differs from the model usually used in studying displacements in alloys through the inclusion of a distance-dependent Ising interaction.

The issue of displacements in alloys has been addressed extensively in the literature [9–11]. More recently, first principles electronic structure calculations have also been used to obtain the relevant parameters for the model Hamiltonian defining the coupling between displacements and configuration degrees of freedom [11,12]. The variables in such a model are $\{\mathbf{u}_i\}$, the displacements at site i, and the occupation or Ising variables, $\{S_i\} = \pm 1$. A displaced Ising variable defined by $S_i = S_i - < S >$ can be used, where $< S >$ measures the average concentration and is zero for a 50-50 alloy. In terms of these variables, the standard model describing binary alloys can be written as [9,12]

$$H = \sum_{i,j}[J_{ij}S_iS_j + \sum_{\alpha\beta}u_{i\alpha}D_{\alpha\beta}(i,j)u_{j\beta} + \sum_{\alpha}K_{\alpha}(i,j)u_{i\alpha}S_j] \tag{1}$$

In this equation, the second term is the elastic energy and the third term describes the *only* coupling between the displacements and the spins. The K_{ij} are the forces induced due to the difference between the two types of atoms [9,12] and the J_{ij} are the pair interactions. This model has been used to analyze pair displacements in alloys [10], and it has been shown that the average pair displacement of sites m and n depend on $< S_m > + < S_n >$. It follows immediately that this model would always predict an AB distance which is *intermediate* between the AA and BB distances; never the shortest or longest. Another feature of this model is that the average separations do not depend on the configurational (chemical) short-range order (the *mean-square* separations do [10]) and there is no direct correlation between the average separations and the ordering or clustering tendency of the solid solution. In contrast, the analysis below will show that such a correlation comes about naturally in the generalized Ising model.

The generalized Ising model differs in one crucial respect from the above model for alloys. The difference lies in the displacement-dependence of the Ising interaction J_{ij}; characteristic of a compressible Ising model:

$$J_{ij} = J_{ij}^0(1 - \epsilon(\mathbf{u}_i - \mathbf{u}_j) \cdot \mathbf{R}_{ij}/|\mathbf{R}_{ij}|) \ . \tag{2}$$

Here, the $\mathbf{R}_{ij}$ are the distances of the undistorted lattice, and the parameter ϵ determines the strength of the coupling to the lattice. The new feature that this introduces into the alloy model is the coupling of displacements to the *relative* spin orientation, S_iS_j which naturally leads to a relationship between static displacements and configurational order. It is clear that the pair displacements predicted by the model defined by Eqs. (1) and (2) will depend on the sign of the Ising interaction [13].

The physics embodied in the compressible Ising model is very simple, it expresses the fact that the interaction between different types of atoms, whether attractive or repulsive, depends on the distance between them. The arguments leading to the linear dependence on displacements in Eq. (2) are very general; (i) it is the leading term in any expansion and should be adequate for small displacements [5] (ii) it would be obtained in an analysis of the type carried out in Cook and de Fontaine [9] or in Gironcoli *et al* [12] if the expansion retains terms which are linear in displacements and quadratic in the spins and, (iii) moreover, it has a microscopic basis in metallic alloys arrived at through the analysis of the ordering behavior in $Cu - Au$ alloys [6,8].

Since the interactions depend on the distance in the generalized Ising model, it seems natural that static displacements accompany chemical correlations. A striking demonstration of this is seen in the triangular lattice antiferromagnet [5] and in its alloy analog, the $L1_0$ structure on a face-centered-cubic lattice. The ordered phases here have the ferromagnetic (like-atom) bonds elongated and the antiferromagnetic (unlike-atom) bonds shortened [6,8]. It would not be a surprise, therefore, to find such correlations in the high temperature disordered phase of an alloy.

It should be emphasized that the generalized Ising model is designed to describe the basic types of interactions in an alloy and the parameters relevant to a particular alloy can be obtained from *ab initio* electronic structure calculations or from embedded atom type approaches [14,15]. All the parameters in the model are expected to depend on the type and

concentration of alloys. The object of this work is to show that the distance-dependence of the Ising interaction leads to qualitatively different behavior of the pair displacements and that these predictions can explain experimental observations.

In the following discussion, it will be assumed that the displacements are being measured with respect to the average lattice including global distortions, wherever they are present. Mechanical equilibrium implies that for a given configuration of spins (chemical configuration of the alloy), the static displacements are those obtained by minimizing the energy. The displacements for a given thermodynamic state can then be obtained by thermally averaging over the spin configurations.

Minimizing the energy given in Eq. (1) with respect to the displacements $\mathbf{u}_i$, and carrying out the statistical averaging leads to the following expression:

$$< \mathbf{u}_m - \mathbf{u}_n > \; = \sum\nolimits_{\mathbf{q}} \{\exp(i\mathbf{q}\cdot\mathbf{R}_m) - \exp(-i\mathbf{q}\cdot\mathbf{R}_n)\}$$
$$\sum_{ij} \exp(-i\mathbf{q}\cdot\mathbf{R}_i) D_{\mathbf{q}}^{-1}(\mathbf{R}_{ij}/|\mathbf{R}_{ij}|)[J_{ij}^0 \epsilon < S_i S_j > + K_{ij} < S_j >] \qquad (3)$$

The size-effect term, involving K_{ij}, is of the exact same form as Froyen and Herring with a cubic symmetry assumed implying that the forces are along the radial direction [16]. This facilitates the comparison between the two models. The elastic properties of the lattice appear in Eq. (3) through the dynamical matrix, $D_{\mathbf{q}}$. All the interaction parameters in the model Hamitonian, Eq. (1), are bare interaction parameters which do not depend on the displacements or the spin configurations. The statistical averages in Eq. (3) are taken with the complete Hamiltonian defined by Eqs. (1) and (2) and include renormalization of these bare parameters which occur naturally in these models. As an example, the effective elastic moduli depend on temperature [5]. In obtaining parameters from microscopic calculations, the natural choice is the parameters of the random solid solution.

It is clear that the Ising interaction and the size-effect term play different roles in determining the static displacements. The crucial difference is that the distance-dependent Ising term leads to a static displacement proportional to the pair-correlation function, the Warren-Cowley short-range order parameter [1]. Analysis of the simplest situation, a random 50-50

alloy with only nearest neighbor interactions, demonstrates these differences. Experiments measure the relative displacements, $u_{mn}^{\mu\nu} =< \mathbf{u}_m - \mathbf{u}_n >^{\mu\nu}$, for a $\mu\nu$ pair situated at sites m and n where the $\mu\nu$ can be AA, BB,or AB for an $A-B$ alloy.

For a random alloy, all the averages in Eq. (3) are zero except the ones involving sites m and n. For this situation, Eq. (3) predicts

$$u_{mn}^{\mu\nu} = 2J^0\epsilon G_{mn} < S_m S_n >_{\mu\nu} + KI_{mn}(< S_m >_{\mu\nu} + < S_n >_{\mu\nu}) \ , \tag{4}$$

where

$$G_{mn} = \sum\nolimits_{\mathbf{q}} D_{\mathbf{q}}^{-1}(\mathbf{R}_{mn}/|\mathbf{R}_{mn}|)(1-\cos\mathbf{q}\cdot\mathbf{R}_{mn}) \ ,$$

K corresponds to K_{ij} where i and j are nearest neighbors, and I_{mn} is exactly the same as that defined in Eq. 20 of Froyen-Herring [10]. The values of the averages for different pairs in the 50-50 alloy are, $< S_m S_n >_{AA}=< S_m S_n >_{BB}= 1$, $< S_m S_n >_{AB}= -1$, and $(< S >_m + < S >_n)_{AA} = 2$, $(< S >_m + < S >_n)_{BB} = -2$, $(< S >_m + < S >_n)_{AB} = 0$.

The size effect term, involving K, leads to a zero relative displacement of A and B atom-pairs in a 50-50 random alloy whereas the Ising term leads to a non-zero static displacement. The results of simulations [3] show that the average AB distances can be quite different from the average lattice spacing in a 50-50 alloy. The simulations of $Cu_{50}Au_{50}$ and $Cu_{50}Ag_{50}$, to be discussed below, also show a nonzero displacement of AB pairs.

Experimental measurements in $Ni_{77.5}Fe_{22.5}$, an ordering alloy, show that the $Ni-Fe$ nearest-neighbor pairs are the closest neighbors in the solid solution. In $Cr_{47}Fe_{53}$, a clustering alloy, the experiments find that the $Cr-Fe$ nearest-neighbor pairs are the farthest apart. These observations are explained naturally by the generalized Ising model if it is assumed that the Ising term is more important than the size-effect term. For these alloys, this is not an unreasonable assumption since the sizes are similar. The experimental values of the nearest-neighbor displacements of the AB pairs in the $NiFe$ and $CrFe$ alloys can be fitted, successfully, to the expression for the displacements, Eq. (3). To simplify the analysis, the short-range order was neglected and the alloys were assumed to be random. The inclusion of the short-range order, which is not very large in the experimental systems,

would change the quantitative values of the interaction parameters but will not affect the qualitative behavior. The parameters obtained from the fitting imply an antiferromagnetic interaction for $Ni_{77.5}Fe_{22.5}$ and a ferromagnetic interaction for $Cr_{47}Fe_{53}$. Specifically, the combination $J^0\epsilon G_{mn}$ is found to be equal to 0.071Å for the $Ni-Fe$ alloy and -0.151Å for the $Cr-Fe$ alloy. The term originating from size effect, KI_{mn}, obtained by fitting the experiments to Eq. 3, is -0.0204Å for the $Ni-Fe$ and 0.0097Å for the $Cr-Fe$ alloy reflecting the fact that Ni is a smaller atom than Fe but Cr is larger than Fe. It is also reassuring to find a smaller size-effect term for $Cr-Fe$ than for $Ni-F$e since the constituents of the former have a smaller size difference.

It should be stressed that without the distance-dependent Ising term, the experimental data cannot be fit at all to the expression, Eq. (3), for the static displacement [1,2].

The alloys studied experimentally, $Ni-Fe$ and $Cr-Fe$, are fairly complicated systems, being transition metal alloys where magnetism is expected to play a role in the ordering. Microscopic models of these alloys, especially their pair correlation functions, are based on the KKR-CPA approach [17]. This approach has been generalized recently to include displacements of atoms [18]. It would be interesting to see if the results of this microscopic approach lead to a description akin to the generalized Ising model presented here and whether the interaction parameters obtained in the by fitting to experiment can be explained on the basis of microscopic interactions.

The connection with the work of Froyen and Herring is evident when the general expression for the displacements is simplied further. To achieve this, two functions need to be defined:

$$F(\mathbf{q}) = \sum_{(ij)} J^0_{ij}\epsilon < S_i S_j > \exp(i\mathbf{q}\cdot\mathbf{R}_{ij})$$

and

$$L(\mathbf{q}) = \sum_{(ij)} \exp(i\mathbf{q}\cdot\mathbf{R}_{ij})$$

In terms of these, the expression for the displacements is,

$$< \mathbf{u}_m - \mathbf{u}_n > \; = \sum_{\mathbf{q}} D^{-1}_{\mathbf{q}} (\nabla_{\mathbf{q}} F(\mathbf{q})) C'_{mn}$$

$$+ \sum_{\mathbf{q}} K D_{\mathbf{q}}^{-1} (\nabla_{\mathbf{q}} L(\mathbf{q})) C''_{mn} \ . \qquad (5)$$

Here, $C'_{mn} = \sum_j [\exp(i\mathbf{q}) \cdot \mathbf{R}_{jm} - \exp(i\mathbf{q} \cdot \mathbf{R}_{jn})]$ and C''_{mn} has a similar definition with the factor in the summation being multiplied by $< S_j >$. Again, in keeping with the work of Froyen and Herring, the size effect term K_{ij} has been assumed to be short-range and $L(\mathbf{q})$ involves only a sum over nearest neighbor shells. If ϵ is set to zero, then Eq. (5) is identical to Eq. 19 of Froyen and Herring [10].

The two terms in the model that are responsible for the static displacement, the compressible Ising and the size-effect term, compete with each other and the AB distance in an ordering alloy does not necessarily come out to be smaller than the AA distance (A is the smaller atom). If K is small, the Ising term dominates and the AB distance indeed turns out to be either the shortest (ordering) or longest (clustering). If the coupling to the lattice, ϵ, is very small then the results from size-effect models are recovered.

One simple class of microscopic models which can deal with both structural and chemical changes is the embedded atom approach which include the formalism of Daw and Baskes [15] and the Effective Medium Theory (EMT) of cohesion in metals [14]. The latter approach has been used to simulate ordering and kinetics of ordering in $Cu - Au$ alloys and shown to lead to a very good description of these phenomena. In the present work, this approach was used to obtain pair displacements in alloys with a large size difference and the results were compared to the predictions of the generalized Ising model.

Simulations based on the EMT model [8,19] were performed to obtain chemically specific average pair displacements in the random solid solutions $Cu_{50}Au_{50}$ and $Cu_{50}Ag_{50}$. The simulations were carried out in a 64 atom cell and the averaging was done over an ensemble of 50 samples. These simulations allowed for global volume changes besides individual displacements of atoms. The results for the nearest and next-nearest neighbor displacements are shown in Tables I and II.

The difference between the ordering and the clustering alloys is clearly seen although the differences are not as striking as that between the $Ni - Fe$ and $Cr - Fe$ alloys. There

is increased competition between the size-effect and the Ising terms in the simulated alloys arising from the larger size difference between Cu and Au or Ag. Fitting the results of the simulations to the compressible Ising model leads to a positive value of the nearest-neighbor J^0, *i.e.* antiferromagnetic interactions for both alloys. The second neighbor interactions are different and is antiferromagnetic for $CuAu$ [20] but ferromagnetic for $CuAg$. The size effect term is larger for the clustering alloy (*cf. Tables I and II*).

The EMT results for the pair displacements are in qualitative agreement with the results obtained from the EAM simulations [3]. Comparing the two sets of results (*cf* Tables I and II), it is seen that the relative differences between displacements of the AA, AB, and BB pairs are very similar in both methods. However, the absolute magnitudes of the displacements are much larger (by nearly a factor of 8) in the EAM simulations. The reason for this is not clear at present.

To conclude, it has been shown that the generalized Ising model provides a natural framework for understanding the correlations between static displacements and chemical short-range order. In particular, it can explain the experimental observation that in ordering alloys, the unlike atoms can be the closest of any nearest-neighbor pair and in clustering alloys they can be the farthest apart. The distance-dependence of the Ising interaction was crucial in obtaining these correlations. This implies that adding this term to the standard model describing displacements in alloys would lead to qualitatively new features in the ordering and phase separating characteristics of alloys. *Ab initio* electronic structure calculations could be used to obtain the parameters in the generalized Ising model thus leading to a microscopic understanding of the interactions.

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[20] The second neighbor antiferromagnetic interaction in $Cu_{50}Au_{50}$ is a characteristic of the EMT interactions and results from the density dependent terms (*cf* Ref. (6)). It can be demonstrated that the groundstate of the compressible Ising model, with first and second neighbor antiferromagnetic interactions, has the $L1_0$ structure characterizing $CuAu$. It should also be emphasized that the EMT interactions do lead to the correct ordering as evident from previous EMT analysis of $Cu - Au$ alloys (Ref. (8) and (19)).

TABLES

TABLE I. Pair-displacements in a random $Cu_{50}Au_{50}$ alloy obtained from simulations based on EMT and the parameters obtained by fitting these displacements to the generalized Ising model. The displacements are measured from the average lattice and the averages are over an ensemble consisting of approximately 50 samples. Approximate EAM results obtained from the plots of Ref. 3 are quoted in parentheses next to the EMT results

	Nearest Neighbor(a. u.)	Next Nearest Neighbor(a. u.)
Cu-Cu	$-0.0109(\simeq -0.08)$	0.004
Cu-Au	$-0.0057(\simeq -0.04)$	-0.004
Au-Au	$0.0233(\simeq 0.16)$	0.005
$J^0\epsilon G_{mn}$(a. u.)	0.012	0.016
KI_{mn}(a. u.)	-0.017	0.0005

TABLE II. Displacements and parameters as in Table 1 but for the $Cu_{50}Ag_{50}$ alloy.

	Nearest Neighbor(a. u.)	Next Nearest Neighbor(a. u.)
Cu-Cu	$-0.0144(\simeq -0.12)$	-0.018
Cu-Ag	$-0.007(\simeq 0.01)$	0.0086
Ag-Ag	$0.0316(\simeq 0.16)$	0.0036
$J^0\epsilon G_{mn}$(a. u.)	0.0156	-0.0128
KI_{mn}(a. u.)	-0.023	-0.011